DIMERIZATION EFFECT ON HF ELIMINATION FROM THE PHOTOIONIZED FLUOROPHENOLS

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A time of flight mass spectrometry study for multi-photon ionization dissociation of monomers and dimers of 2- and 3-fluorophenols (2FP and 3FP) by a pulsed UV laser light of wavelength 266 nm will be presented. For these molecules, HF elimination from the excited and ionic states is a vital reaction channel. Our measurements reveal that the reaction does not occur from the monomer of 3FP, but it does occur with a measurable yield from the monomer cation of 2FP. On the other hand, upon formation of hydrogen bonded dimers, this reaction is triggered in the cation of 3FP, but for 2FP dimer cation the reaction is so facile that no intact dimer cation survives and only the HF eliminated dimer ion shows up in the mass spectrum. Electronic structure theory predicts that in the D_0 state of 2FP dimer cation, HF elimination is exothermic, but the process encounters a large barrier, 2.75 eV. However, in S_1 state of the dimer the reaction is predicted to be barrierless. Thus, we propose that for this dimer, HF elimination takes place in the intermediate S_1 state, and the remaining fragment that has relatively lower ionization energy is ionized effectively by an overall two-photon (1+1) process. For the reaction to occur from 3FP dimer cation, a rearrangement of the dimer geometry and formation of an intermediate adduct has been suggested, and it is argued that the latter could be produced by nucleophilic attack of the neutral moiety at the ortho site of the cationic counterpart, and the whole process requires 3-photon (2+1) absorption.